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Dedicated to Professor Hisashi Odani On the
Occasion of His Retirement)

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Study on Photo-induced Colour Reversion of Stoneground Wood Pulp by FT-IR Spectroscopy

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The photo-induced colour reversion of handsheets of unbleached and bleached stoneground wood pulp was studied by FT-IR transmission spectroscopy. Change in the chemical structure of thin handsheets were monitored quantitatively as a function of repeated exposures to UV irradiation at 320 nm followed by storage in the dark. A slight loss of carbohydrate structures was observed throughout the cycles, while a pronounced loss in lignin aromaticity was produced by the UV irradiation. For the unbleached sample, irradiation initially caused the preferential destruction of non-etherified (free) phenolic groups. The bleached samples, with a higher initial content of non-etherified groups, showed preferential destruction of etherified groups throughout the irradiation cycles. A rapid initial decrease in α -carbonyl group content occurred for both bleached and unbleached samples; non-conjugated carbonyl group content increased with irradiation.

KEYWORDS: Fourier Analysis / Infrared Spectroscopy / Transmission / Colour Reversion / Stoneground Wood / Ultraviolet Radiation / Radiation Effects / Pulps / Lignins / Cellulose

Introduction

The use of mechanical wood pulps in a number of applications is limited because of their rapid loss of brightness. Some understanding of the chemical changes responsible for brightness loss is required if this colour reversion is to be minimized. The chemical changes responsible for colour reversion are difficult to determine *in situ*, in part because of the relatively small chemical changes that are occurring in the heterogeneous and complex fibre surface matrix. A variety of infrared spectroscopic techniques¹⁻⁵⁾ have been applied to the problem. The difficulty of detecting the small IR spectral change during reversion is compounded by the variability in composition from point to point on the paper surface.

In this study, the effects of non-uniformity of the sample were minimized by using the same spot on the sample for both the irradiation and IR measurements. This facilitated a quantitative analysis of the chemical alteration of the pulps during irradiation and storage. Furthermore, the sheet was irradiated with a narrow band of light centred at 320 nm, in order to simplify the initial photochemical processes. The maximum in the action spectrum for brightness loss occurs close to this wavelength.⁶⁾ The spectra were measured in trans-

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mission mode on very thin sheets of bleached and unbleached stoneground wood pulp.

Experimental

Sample preparation:

The samples were very thin handsheets ($\sim 10 \text{ g/m}^2$) of unbleached and commercial alkaline peroxide bleached stoneground wood (SGW) from a Norwegian spruce furnish. Each sample sheet was pressed by a pellet maker die with a pressure of 10 tons to obtain a transparent sample, which was then fixed in an IR sample holder.

IR measurement, UV irradiation and storage cycles:

Figure 1 illustrates a series of cycles: each cycle consists of an IR measurement, UV irradiation for 30 min, and one day storage, except the 5th cycle where an 8-day storage was employed without irradiation. After the final cycle, an additional IR measurement was performed.

The IR spectra were obtained with a Nicolet 7199 spectrometer equipped with a liquid-nitrogen cooled MCT detector. One thousand scans were acquired and the resolution was 2 cm^{-1} . UV irradiation was performed with a 450-W Xenon lamp, and the monochromator of a SPEX spectrofluorometer equipped at a wavelength of 320 nm. During the irradiation, the sample was kept fixed in the IR sample holder in order to ensure that exactly

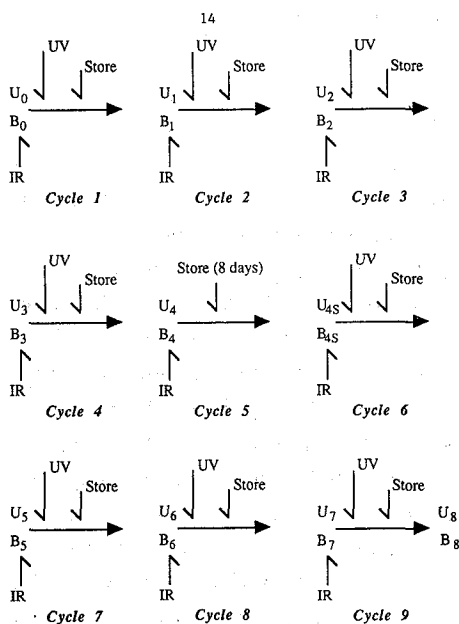


Figure 1. Sequence of UV irradiation and IR measurements. U and B stand for handsheets of unbleached and bleached SGW. UV and IR signify UV irradiation and IR measurement. The samples were irradiated for 30 min, then stored for 1 day, except in Cycle 5, where the samples were stored for 8 days without irradiation.

the same spot was used for the IR measurement and UV irradiation. The irradiated sample, fixed in the IR holder, was stored in a desiccator. There was no significant difference between two spectra obtained before and after one day storage, indicating that the effect of short-term storage on the chemical changes is very small.

The intensities of 10 spectra obtained for a series of UV exposure cycles for the unbleached sample can be compared directly because the same spot was used each time. Also, a direct comparison of the intensities for the bleached sample is possible for the same reason. However, the spectra of the unbleached and bleached samples cannot be compared; there is no suitable reference peak in the spectra because all of the three main components (lignin, cellulose and hemicellulose) probably underwent some changes during the bleaching process.

Results and Discussion

Figure 2 shows the spectrum of the non-irradiated unbleached sample, U_0 . We monitored the change in peak height of the following peaks during irradiation and storage: 1662, 1637, 1509, 1452, 1426, 1371, 1336, 1318, 1265, 1232, and 1060 cm^{-1} . The peak at 1723 cm^{-1} , which appeared during sample irradiation, was also monitored.

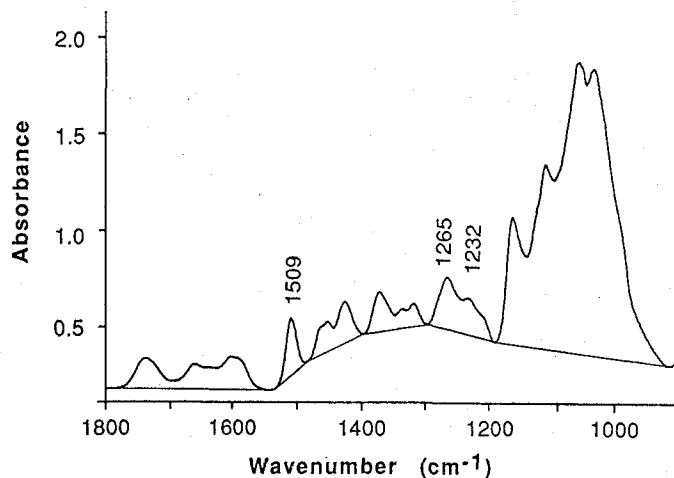


Figure 2. An IR spectrum of non-irradiated unbleached stoneground wood, U_0 . The baselines from which peak heights were calculated are shown.

Comparison between non-irradiated and irradiated samples:

Figures 3A and 3B show the absorbance changes for the 1509 cm^{-1} and 1060 cm^{-1} bands, respectively, against the elapsed time as well as the cycle number. The amounts of lignin and carbohydrates (cellulose and hemicellulose) can be estimated from these peaks. The lignin content in pulp and paper is usually estimated by the peak height at 1509 cm^{-1} ,^{7,8)} which is assigned to benzene ring vibration, because the absorption coefficient of

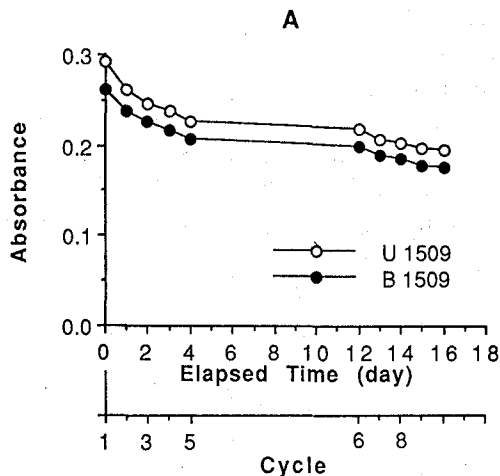


Figure 3A. Band intensity changes for the lignin peak at 1509 cm^{-1} against elapsed time and irradiation cycle, as defined in Fig. 1. Bleached and unbleached samples are of different thicknesses, so intensities are not comparable.

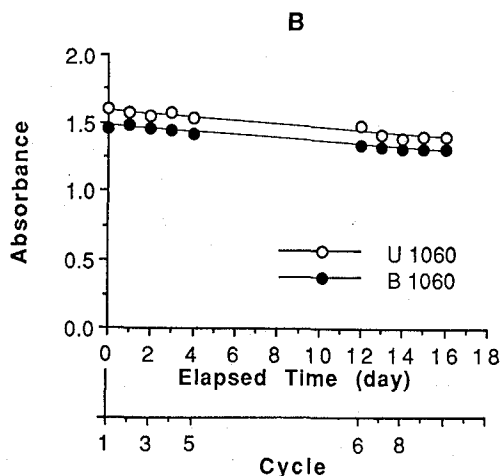


Figure 3B. Band intensity changes for the carbohydrate peak at 1060 cm^{-1} against elapsed time and irradiation cycle, as defined in Fig. 1. Bleached and unbleached samples are of different thicknesses, so intensities are not comparable.

this peak is not influenced by substitution.⁹⁾ In this study, the lignin content was estimated using this peak. The carbohydrate content was estimated using the peak at 1060 cm^{-1} which is assigned to C-C and C-O stretching in cellulose,^{10,11)} overlapped by the same peaks in hemicellulose.¹²⁾ Although the absorbance decreases with the elapsed time for both the lignin and carbohydrates, the pattern of the decrease is different. A pronounced loss of lignin aromaticity is observed during irradiation, while a slight loss of carbohydrates is

observed throughout the cycles. The unbleached and bleached samples show a similar trend.

Figures 4A and 4B show the absorbance change for peaks at 1265 and 1232 cm^{-1} , and at 1452, 1426, 1371, 1336, and 1318 cm^{-1} against elapsed time. The former two peaks may be assigned to the lignin guaiacyl ring breathing with ether CO- stretching,⁹⁾ while the latter five peaks may be assigned to carbohydrates. The pattern for the absorbance change of the two peaks in Fig. 4A is almost identical to the change for the lignin 1509 cm^{-1} peak in Fig. 3A. Therefore, these peaks are assigned to lignin, although they may overlap with

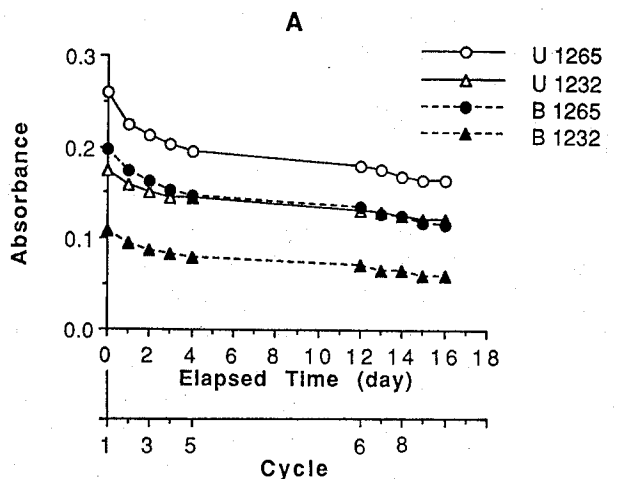


Figure 4A. Band intensity changes at 1265 and 1232 cm^{-1} against elapsed time and irradiation cycle.

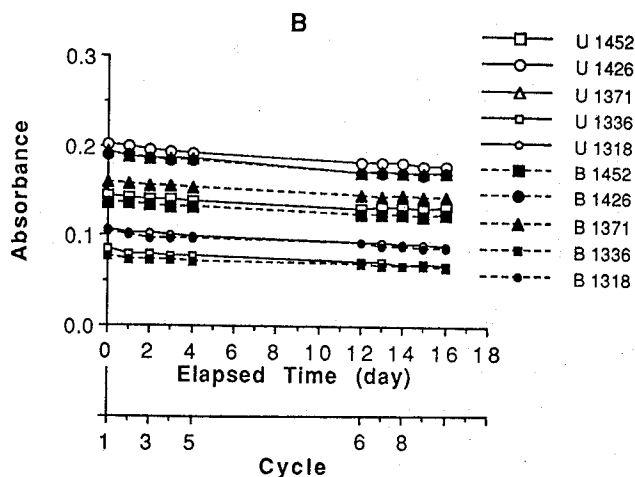


Figure 4B. Band intensity changes at 1452, 1426, 1371, 1336, and 1318 cm^{-1} against elapsed time and irradiation cycle.

the peaks for carbohydrates appearing between 1300 and 1200 cm^{-1} : cellulose I, the main component of wood cellulose, has five weak peaks and a medium peak at 1280 cm^{-1} ,¹³⁾ and hemicellulose has also a weak peak around 1250 cm^{-1} .¹⁴⁾ On the other hand, the pattern of absorbance changes in Fig. 4B is almost the same as the band at 1060 cm^{-1} (Fig. 3B) for carbohydrates. Therefore, these peaks are assigned to carbohydrates, though the peaks of the CH_3 and CH_2 deformation and the benzene ring vibration of lignin exist around 1452 and 1426 cm^{-1} , respectively.⁹⁾

Figure 5 shows the dependence of the peak ratio of 1232 to 1265 cm^{-1} on elapsed time for the unbleached and bleached samples. Sarkanen et al.¹⁵⁾ observed in their study of lignin model compounds that the intensity of the 1232 cm^{-1} band increases at the expense of the intensity of the 1265 cm^{-1} band during methylation of the C4 position of the guaiacyl structure. Therefore, the intensity ratio of 1232 cm^{-1} to 1265 cm^{-1} is regarded as a measure of the ratio of etherified to non-etherified structures in lignin. This assumption was supported by our recent solid-state NMR study.¹⁶⁾ The ratios for the unbleached and bleached samples are clearly different (Fig. 5). In the case of the unbleached sample, the ratio increases during the first four cycles, then remains constant. This observation indicates a more pronounced decrease in the non-etherified structure than the etherified structure in the initial stages of the irradiation, followed by the same rate of decrease for both structures. On the other hand, in the case of the bleached sample, the ratio decreased gradually throughout the cycles, indicating that the etherified structure decreased at a faster rate than the non-etherified structure from the beginning to the end of the experiment. The calculated ratios of 1232 cm^{-1} to 1265 cm^{-1} are 0.67, 0.73, 0.55, and 0.52 for U_0 , U_8 , B_0 , and B_8 , respectively. The order of the ratios is $\text{U}_8 > \text{U}_0$ for the unbleached sample and $\text{B}_0 > \text{B}_8$ for the bleached sample. This indicates that, during the irradiation, the non-etherified structure decreased more than the etherified structure in the unbleached sample, while the etherified structure decreased more in the bleached sample. This observation is

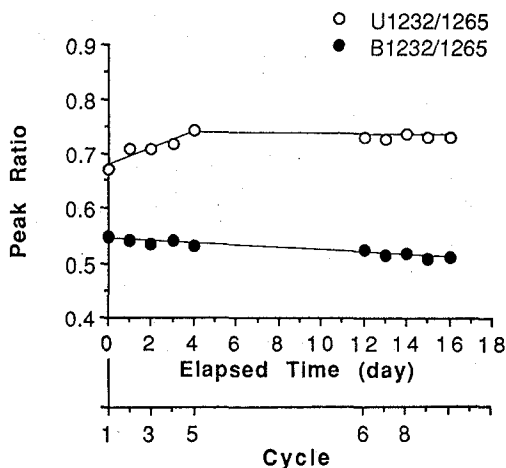


Figure 5. The dependence of peak ratio 1232/1265 cm^{-1} on elapsed time and irradiation cycle.

in agreement with our previous solid state NMR results.¹⁶⁾

In Figure 6 the change in absorbance at 1723 cm^{-1} is plotted against elapsed time. This band, which overlaps the band around 1739 cm^{-1} assignable to the ester group of hemicellulose,^{5,17)} begins to appear in the subtraction of U_n ($n=1,2,\dots,8$) from U_0 , or the subtraction of B_n from B_0 . It is assigned to the non-conjugated carbonyl vibration of carboxyl, aldehyde, and/or ketone functionalities. The intensity of this band increased with irradiation, but did not change with the 8-day storage, and thus was produced only by the irradiation.

Figure 7 shows the intensity change for the peak at 1662 cm^{-1} , assigned to α -carbonyl stretching vibration,⁹⁾ against the elapsed time. The peak height of the 1662 cm^{-1} band was determined from the subtraction spectra U_0-U_n and B_0-B_n ($n=1-8$). In contrast to the non-conjugated carbonyl groups, the peak height decreased drastically during the first two cycles and no significant change was observed afterwards. This indicates that the con-

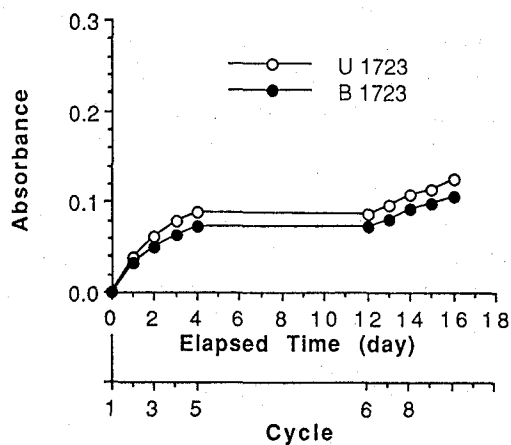


Figure 6. Band intensity changes at 1723 cm^{-1} against elapsed time and irradiation cycle.

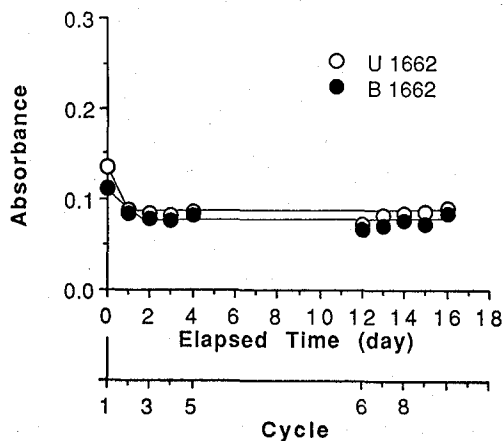


Figure 7. Intensity change of the peak at 1662 cm^{-1} during irradiation and storage.

sumption of the α -carbonyl groups occurred in the early stages of the irradiation. A similar observation was reported by Michell et al.³⁾ in their study of photo-induced colour reversion of chemimechanical pulps. According to a reaction pathway for photo-induced colour reversion,¹⁸⁾ creation of α -carbonyl radicals takes place in the initial stages of the reversion. Some of these radicals return to their initial stable state, while others are consumed in reaction of the α -carbonyl groups.¹⁹⁾ The rapid decrease of the α -carbonyl groups observed in Figure 7 might reflect this consumption. Under other conditions, an increase in α -carbonyl content during irradiation has been observed.^{16,20)} The reasons for this apparent difference are under investigation.

The peak height of the 1637 cm^{-1} band changed in the same way as that of the 1662 cm^{-1} band for both unbleached and bleached samples, but, unfortunately, this peak could not be assigned. Michell et al. assigned this peak to water absorbed on the paper, or to quinones or keto groups conjugated with more than one aromatic ring.⁴⁾ In fact, a broad band of absorbed water does overlap in this region. However, since the moisture content was kept constant in our experiment, the peak could not be assigned to absorbed water.

In this study we could not obtain positive evidence for the creation of quinone groups²¹⁾ due to irradiation. Although quinones have two peaks around 1660 and 1600 cm^{-1} , we observed a decrease in peak height around both these wavelengths.

Effect of storage:

During storage, neither the α -carbonyl nor non-conjugated carbonyl structures underwent any significant changes. On the other hand, both the lignin and carbohydrates showed a slight decrease, presumably due to oxidation. The effect of the storage showed the same tendency for the unbleached and bleached samples.

Comparison between unbleached and bleached samples:

The ratio of the peak height at 1739 cm^{-1} to the peak height at 1060 cm^{-1} (the ester groups of hemicellulose^{5,17)} to carbohydrates) is much smaller in B₀ than in U₀. This observation indicates that cleavage of the ester bands of O-acetylgalactoglucomannan,²²⁾ an abundant component of softwood hemicelluloses, occurred during the bleaching process.

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